Supporting Information

Branched Polymeric Media: Perchlorate-Selective Resins from Hyperbranched Polyethyleneimine

Dennis P. Chen[1], Changjun Yu[2, 3], Ching-Yu Chang[2], Yanjian Wan[2], Jean M. J. Frechet[4,5], William A. Goddard III[6,1] and Mamadou S. Diallo[1, 3]*

[1]Graduate School of Energy, Environment, Water and Sustainability (EEWS)
Korea Advanced Institute of Science and Technology (KAIST)

[2]AquaNano, LLC

[3]Environmental Science and Engineering
Division of Engineering and Applied Science
California Institute of Technology

[4]Department of Chemistry
University of California, Berkeley

[5]Physical Science and Engineering Division
King Adullah University of Science and Technology

[6]Materials and Process Simulation Center
Division of Chemistry and Chemical Engineering
California Institute of Technology

* To whom all correspondence should be addressed.
E-mail: mdiallo@kaist.ac.kr and diallo@wag.caltech.edu

The supporting information (SI) provides a detailed description of all the methods and procedures that were used to synthesize the new resins described in this study. The SI also includes supporting tables and figures.

I. Resin Synthesis

All base polyethyleneimine (PEI) resins were synthesized using an inverse suspension of water-in-toluene stabilized by a surfactant. The PEI resins were subsequently reacted with alkylating reagents to produce resins with quaternary ammonium chloride (Cl^-) exchange sites (QPEI). Tables 2S and 3S list the base PEI and QPEI resins synthesized in this study. The synthetic procedures and corresponding reaction schemes are described below.

I. 1. Chemicals

Reagent grade chemicals (> 98 wt%) were used to synthesize all PEI and QPEI resin beads. Deionized (DI) water (minimum resistivity 18MΩ) was obtained from a Milli-Q filtration unit. Anhydrous sodium chloride (NaCl) was purchased from Alfa Aesar. Concentrated hydrochloric acid (12 N) was purchased from EMD. Branched polyethyleneimine (PEI) macromolecules [SP-200 with molecular weight M_n = 10,000 and SP-018 with M_n = 1800] were purchased from Nippon Shokubai Co., Ltd. Sulfonic 100 (branched dodecyl benzene sulfonic acid, 97%) was purchased from the Stepan Company. Methyl iodide (MeI), bromoethane, 1-bromopropane, 1-bromobutane, 1-bromo-2-methylpropane, 1-bromo-3-chloropropane (BCP), diisopropylethylamine (DIPEA) and epichlorohydrin (ECH), were purchased from Sigma-Aldrich. Methanol (MeOH), ethanol (EtOH), toluene, isopropanol (IPA), and sodium hydroxide (NaOH) were purchased from Mallinckrodt Chemicals. All chemicals were used as received.

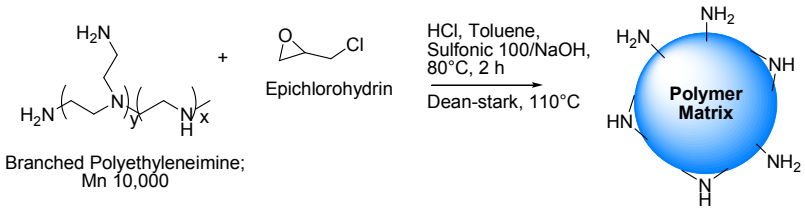
Comment [D.C.1]: Not used

I. 2. Synthesis of base PEI resins

Equipment: 1-L or 500-mL round bottom flask equipped with a mechanical overhead stirrer, a thermometer, a reflux condenser, an addition funnel, and an inert gas port.

I.2.A. ECH crosslinked PEI resins

Scheme 1S:

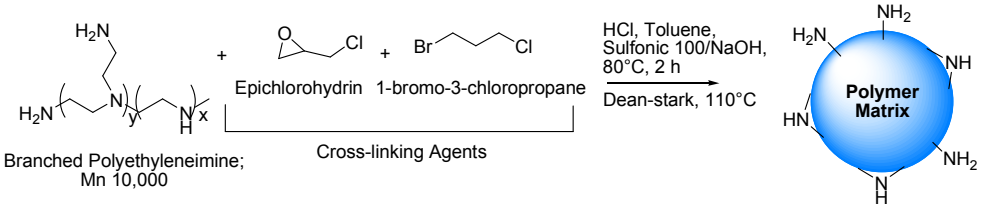


PEI-1, **PEI-2**, **PEI-3** and **PEI-4**: What follows is a typical procedure for preparing ECH crosslinked PEI beads. A solution of 8.5 g of HCl (36-38 wt%) in 15 g of DI water was added to the reaction flask containing 15 g of PEI over a course of 10 min at room temperature under nitrogen. Then 50 mg of Sulfonic 100 in 1.1 M NaOH was added to the vessel, followed by the addition of 125 mL of toluene. The oil bath temperature was then brought to 70-80 °C. In a separate vessel, 15 g of ECH toluene solution (40 wt%) was prepared. The ECH solution was added drop-wise to the reaction mixture over a 60 min period. The

reaction was continued for an additional 2 h. Following this, the dehydration of the reaction mixture was initiated using a Dean stark apparatus at a temperature of 110 °C. The reaction end point was reached when all the water from the system had been removed. After cooling to ambient temperature, the resins were collected by filtration over a Büchner funnel and were cleaned by washing with methanol and neutralized with saturated sodium bicarbonate. The beads were then sequentially washed with EtOH and a mixture of EtOH (50 vol%) and DI water. Following this, the beads were filtered off and stored at room temperature. PEI resins with NCR of 20 wt% (**PEI-1**), 33 wt% (**PEI-2**), 55 wt% (**PEI-3**) and 67 wt% (**PEI-4**) were prepared by following the aforementioned procedure. For convenience, the degree of crosslinking is quoted as the wt% of crosslinker used to prepare the resin. ECH crosslinked PEI resin beads with different average diameters were prepared using similar conditions as **PEI-2**, but with different suspension stirring rates. Stirring rates were, respectively, equal to 175, 200, 225, and 250 rpm during the preparation of **PEI-2,1'**, **PEI-2,2'**, **PEI-2,3'**, and **PEI-2,4'**, respectively. **PEI-2,5'** was prepared using a branched PEI with molar mass (M_n) of 1800 and following the same protocol as **PEI-2**.

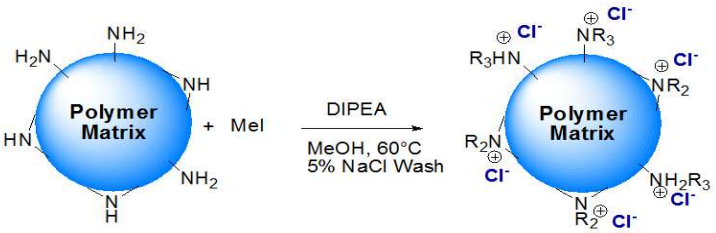
I.2.B. ECH/BCP cross-linked resin

Scheme 2S:



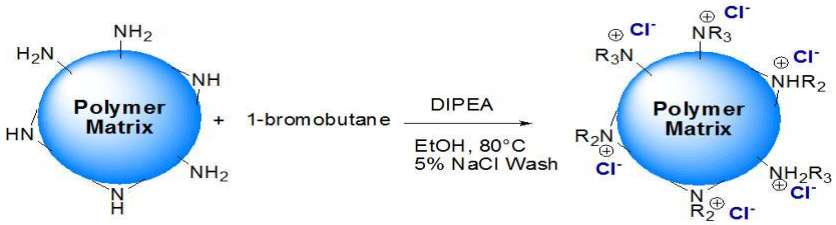
PEI-5: A solution of 34 g of HCl (36-38 %) in 60 g of DI water was added to the reaction flask containing 60 g of PEI over a course of 20 min at room temperature under nitrogen. Then a solution of 200 mg of Sulfonic 100 in 1.1 M NaOH was added to the vessel, followed by the addition of 450 mL of toluene. The oil bath temperature was then brought to 70-80 °C. In a separate vessel, 13.8 g of ECH + 30 g of BCP in a toluene solution (90 mL) was prepared. The ECH/BCP solution was added to the reaction mixture over a 60 min period. The reaction was continued for an additional 2 h. Following this, the dehydration of the reaction mixture was initiated using a Dean stark apparatus at a temperature of 110 °C. The reaction end point was reached when all the water from the system had been removed. After cooling to ambient temperature, the resins were cleaned following the same procedure that was used to clean the ECH cross-linked PEI resins. Following this, the beads were filtered off and stored at room temperature. **PEI-6** was prepared following the procedure used to prepare **PEI-5**. However, the amount of mixed crosslinker was equal to 23 g of ECH + 50 g of BCP.

I. 3. Preparation of quaternized resin QPEI-1.
Scheme 3S:



QPEI-1: 50 mL of MeOH was added into a 250 mL pressure vessel containing 25 g of Büchner dried **PEI-6**. Then 80 g of MeI and 20 mL of DIPEA was added to the mixture. The reaction mixture was stirred and heated to 60 °C in a temperature-controlled oil bath for 6 h to afford **QPEI-1**. After cooling to room temperature, the resins were collected by filtration over a Büchner funnel. The resins were washed successively in a fritted glass column with MeOH (1L/10g of resin) to remove organic reagents and byproducts, and then with DI water (1L/10g of resin). The resins were converted to chloride form by washing successively with 1.0 N HCl (1L/10g of resin), DI water until the pH of the eluate was neutral, 5 wt% NaCl (1L/10g resin), and again with DI water (1L/10g resin) or until the conductivity of the eluate was equal to that of DI water.

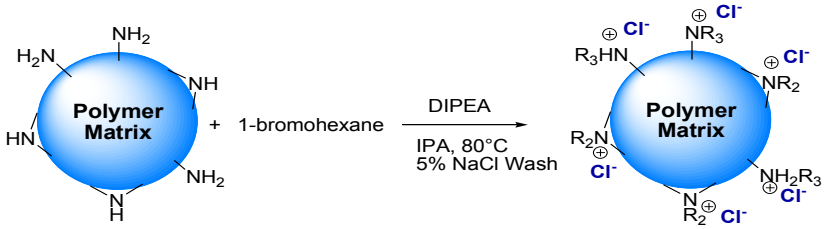
I. 4. Preparation of quaternized resin QPEI-2.
Scheme 4S:



QPEI-2: 50 mL of EtOH was added into a 250 mL pressure vessel containing 25 g of Büchner dried **PEI-6**. 100 g 1-bromobutane and 20 mL of DIPEA was added to the mixture. The reaction mixture was stirred and heated in a temperature-controlled oil bath to 80 °C for 24 h to afford **QPEI-2**. After cooling to room temperature, the resins were collected by filtration over a Büchner funnel. The resins were washed successively in a fritted glass column with the same cleaning procedure used for **QPEI-1**.

I. 5. Preparation of quaternized resin with hexyl group (QPEI-3).

Scheme 5S:

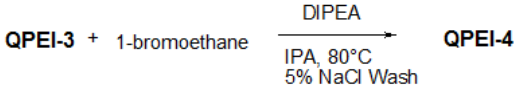


QPEI-3: 75 mL of IPA was added into a 250 mL pressure vessel containing 25 g of Büchner dried **PEI-6**. 100 g 1-bromohexane and 20 mL of DIPEA was added to the mixture. The reaction mixture was stirred and heated for 24 hour to 80 °C in a temperature-controlled oil bath. After cooling to room temperature, the resins were collected by filtration over a Büchner funnel. The same cleaning procedure was employed as previously described for **QPEI-1**.

I. 5. Preparation of quaternized resin with hexyl groups (QPEI-1H, QPEI-2H, QPEI-3H, QPEI-4H, QPEI-5H). These resins were prepared following the procedures used to prepare **QPEI-3**. **PEI-1**, **PEI-2**, **PEI-3**, **PEI-4**, and **PEI-5** were employed, respectively, as precursor resins for the functionalization of **QPEI-1H**, **QPEI-2H**, **QPEI-3H**, **QPEI-4H,** and **QPEI-5H**. **QPEI-1H**, **QPEI-2H**, **QPEI-3H**, and **QPEI-4H** were used to assess the effect of the nominal crosslink ratio on ClO_4^- sorption (Figure 2). **QPEI-5H** was compared with **QPEI-2H** to study the effect of cross-linker chemistry on ClO_4^- sorption (Figure 3).

II. 6. Preparation of quaternized resin with hexyl/ethyl groups (QPEI-4)

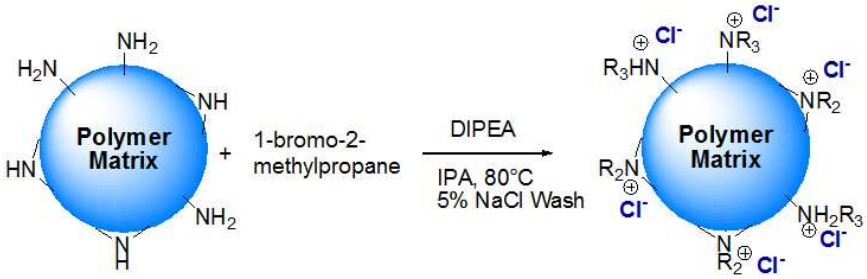
Scheme 6S:



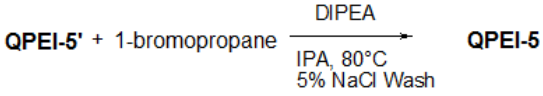
QPEI-4: 40 mL of IPA was added into a 250 mL pressure vessel containing 25 g of Büchner-dried resin **QPEI-3**. Then 50 g of 1-bromoethane and 20 mL of DIPEA was added to the mixture. The reaction mixture was stirred and heated to 80 °C in a temperature-controlled oil bath to 80 °C overnight for 24 h to afford **QPEI-4**. After cooling to room temperature, the resins were collected by filtration over a Büchner funnel. The resins were washed in the same manner as **QPEI-1**.

II. 7. Preparation of quaternized dual alkylated resin QPEI-5

Scheme 7AS:



Scheme 7BS:



QPEI-5: 75 mL of IPA was added into a 250 mL pressure vessel containing 25 g of Büchner dried **PEI-6**. 80 g of 1-bromo-2-methylpropane and 20 mL of IPA was added to the mixture. The reaction mixture was stirred and heated 24 h to 80 °C in a in a temperature-controlled oil bath to afford **QPEI-5'**. The supernatant was then decanted and 75 mL of IPA was added to **QPEI-5'**. Then 50 g of 1-bromoethane and 20 mL of DIPEA was added to the mixture. The reaction was stirred and heated to 80 °C in temperature-controlled oil bath for 24 h to afford **QPEI-5**. The work-up procedure follows the protocol used for **QPEI-1**.

Table 1S. Selected Properties of Perchlorate and Related Anions.				
Anion	[a]Ionic Radius (Å)	[b]Size-to-Charge Ratio	[a]Hydration Free Energy (kJ/mol)	[c]Shape
ClO_4^-	2.40	2.4	-259	Tetrahedral
TcO_4^-	2.50	2.5	-245	Tetrahedral
Cl^-	1.72	1.72	-340	Spherical
NO_3^-	1.96	1.96	-300	Trigonal Planar
HCO_3^-	1.56	1.56	-335	Trigonal Planar
SO_4^{2-}	2.30	1.15	-1295	Tetrahedral

[a]Data compiled by Moyer, B. A. and Bonnesen, P. V. Physical factors in anion separations. In *Supramolecular Chemistry of Anions*. Bianchi, A.; Bowman-James, K. and Garcia-Espana, E. Ed.; Wiley-VCH, New York, 1997, pp. 1-44.

[b]Equal to the ratio of the charge of the anion to its ionic radius.

[c]Geometrical arrangements of anions taken from Gloe, K.; Stephan, H. and Grotjahn, M. Where is the anion extraction going? *Chem. Eng. Technol*. **2003**, 26,1107-1117.

Table 2S: List of Base PEI Resins that Were Synthesized in This Study

Sample ID	Crosslinker	Water content (%)	Nominal crosslink ratio (wt%)
PEI-1	ECH	67.3	20
PEI-2	ECH	58	33
PEI-3	ECH	39.4	55
PEI-4	ECH	43.9	67
PEI-5	ECH + BCP	65.4	41 with a BCP:ECH molar ratio of ~1.3:1.
PEI-6	ECH + BCP	58.6	51 with a BCP:ECH molar ratio of ~1.3:1

Table 3S: List of Quaternized PEI Resins (QPEI) That Were Synthesized in This Study

Sample ID	Precursor	Nominal crosslink ratio (wt%)	$SBEC_v$ (mequiv/mL)	Functional group	Water content (%)
QPEI-1H	PEI-1	20	1.03	Hexyl	61
QPEI-2H	PEI-2	33	1.26	Hexyl	40.1
QPEI-3H	PEI-3	55	1.34	Hexyl	39
QPEI-4H	PEI-4	67	1.36	Hexyl	35
QPEI-5H	PEI-5	41	1.32	Hexyl	35
QPEI-1	PEI-6	51	2.7	Methyl	41.8
QPEI-2	PEI-6	51	1.8	Butyl	38.5
QPEI-3	PEI-6	51	0.9	Hexyl	27
QPEI-4	PEI-6	51	1.4	Hexyl & Ethyl	25
QPEI-5	PEI-6	51	1.23	Butyl &Propyl	38

Figure 1S. FT-IR Spectra of the Base PEI Resin with Mixed BCP/ECH Crosslinkers (PEI-6) and the QPEI Resins with Hexyl Groups (QPEI-3) and Mixed Hexyl + Ethyl Groups (QPEI-4).

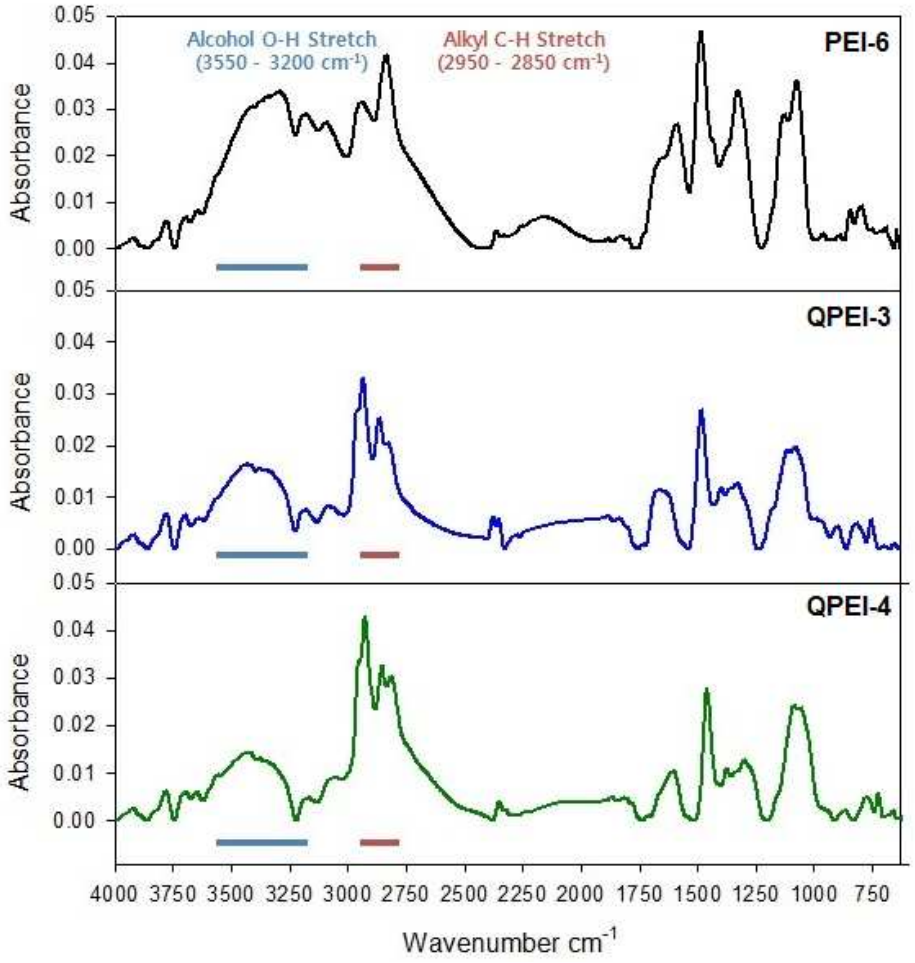
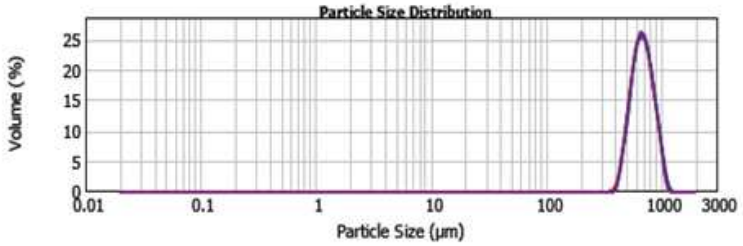


Figure 2S. Particle Size Distributions for the Base PEI Resin (PEI-6) and Purolite A-530E Resin.

A. Base PEI-6 Resin [Mean Particle Diameter (D_{50}) = 694 µm]



B. Purolite A-530E Resin [Mean Particle Diameter (D_{50}) = 635 µm]

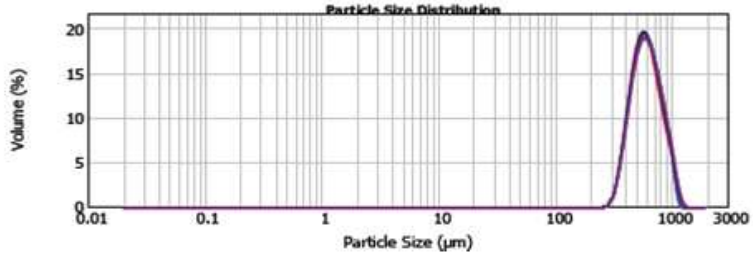


Figure 3S. SEM Micrographs of the Purolite A-530E Resin (A) and the Base PEI Bead with Mixed ECH/BCP Crosslinker (PEI-6) Resin.

A. **B**

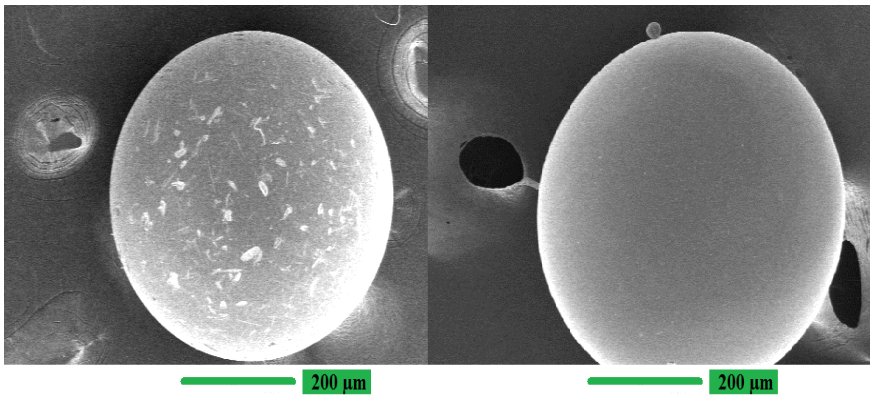


Figure 4S. Sorption Isotherms of ECH Crosslinked PEI Resins with Hexyl Ammonium Chloride as a Function of Nominal Crosslink Ratio. The percentages indicate the nominal crosslink ratios of the resins. In these experiments, 0.025, 0.050, and 0.10 g of media (dry-weight) were contacted with 625 ppb ClO_4^- in Redlands makeup water for 24 h.

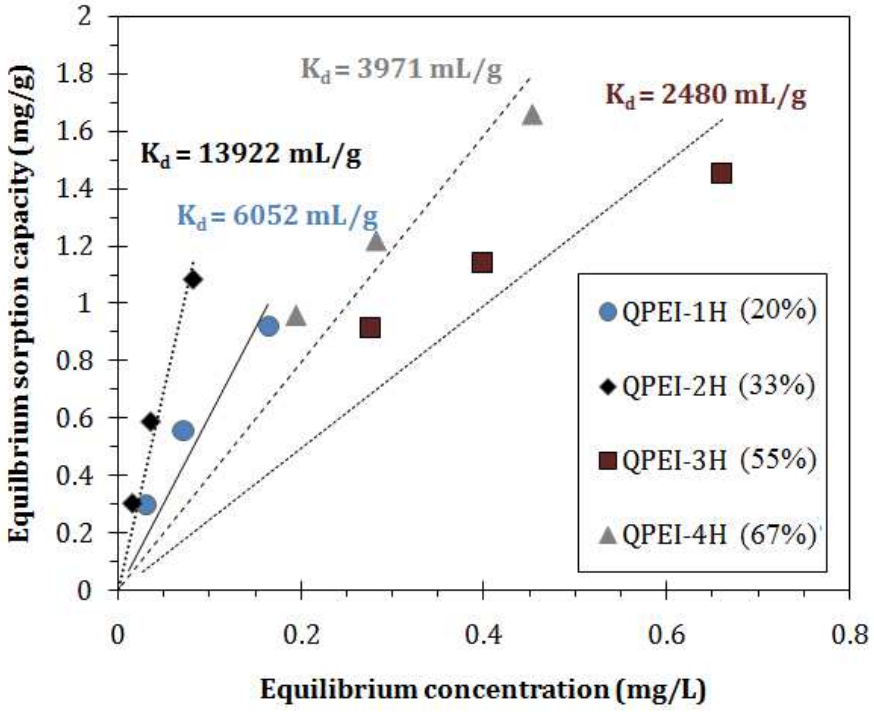
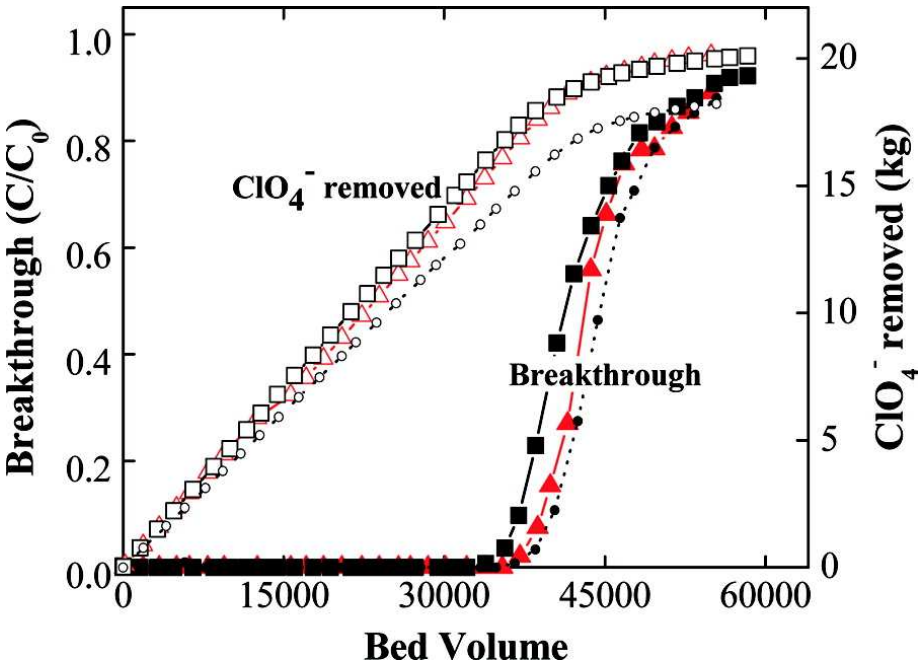


Figure 5S. Perchlorate Breakthrough Curves for the A-530E Resin During Field Tests at the Rancho Cordova Groundwater Site[1]. The data was taken from Gu et al[2]. Treatment of Perchlorate-Contaminated Groundwater Using Highly Selective, Regenerable Ion-Exchange Technologies. *Environ. Sci. Technol.* **2007**, 41, 6277-6282.



[1]Breakthrough curves (solid symbols) and mass removal of perchlorate (open symbols) after treatment and regenerations using the tetrachloroferrate displacement technique. The triangle and square symbols represent the third and fourth treatment and regeneration cycles, which compared favorably with the initial breakthrough and perchlorate removal (circles) The influent concentration was 830−890 μg/L ClO4-, and the flow rate was 1BV/min.

[2]Gu et al. reported that "*the bifunctional resin (Purolite A-530E) treated about 37 000 empty bed volumes (BVs) of groundwater before a significant breakthrough of perchlorate occurred at an average flow rate of 150 gpm (or 1 BV/min) and a feed perchlorate concentration of about 860 μg/L*".